Multiscale microkinetic modelling of carbon monoxide and methane oxidation over Pt/γ-Al₂O₃ catalyst
L. Montesano¹, P. Lott¹, L. Maier², S. Tischer², S. Angeli¹, O. Deutschmann¹,²*

Introduction and goals
- Emissions from vehicles contain many harmful components - must be efficiently converted.
- Improvements of the catalyst require the knowledge of the microkinetics, but the complexity of the exhaust gas mixture makes it very challenging to unravel them.
- The catalyst has been shown to undergo modiﬁcations under the highly dynamic operation of the catalytic converters [1, 2].

Microkinetic mechanisms present in literature are assessed through the simulation of dynamic experimental campaigns (light – off curves) performed in very different operative conditions.

Understanding what are the key parameters suitable for a dynamic description of the catalyst:
- First attempt: \( F_{\text{cat/geo}} \). Starting from the characterization of the fresh and fully reduced catalyst, the value is optimized in order to reproduce the experimental data in the ignition area.

### CO oxidation

<table>
<thead>
<tr>
<th>Microkinetic models</th>
<th>Thermodynamic consistency</th>
<th>Reaction pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chan et al. [3]</td>
<td>Yes, 0 – 1000 °C</td>
<td>Molecular, Dissociative, LHHW, EIR, LHHW</td>
</tr>
<tr>
<td>Mhadeshwar et al. [4]</td>
<td>Yes, 0 – 1400 °C</td>
<td>Molecular, Dissociative, LHHW</td>
</tr>
</tbody>
</table>

### CH₄ oxidation

<table>
<thead>
<tr>
<th>Microkinetic models</th>
<th>Thermodynamic consistency</th>
<th>Reaction pathways</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koop et al. [5]</td>
<td>Yes, 150 – 600 °C</td>
<td>Dissociative, Dissociative, Pyridic, Oxidative dehydrogenation</td>
</tr>
<tr>
<td>Quiceno et al. [6]</td>
<td>No</td>
<td>Dissociative, Pyridic, Oxidative dehydrogenation</td>
</tr>
</tbody>
</table>

**Fig. 1:** CO oxidation light-off curves. A) Packed-bed reactor with the following inlet conditions: 1000 ppm CO, 8% O₂, N₂ balance, GHSV = 36430 1/h. Simulations using DETCHEM°geo [7]. B) Monolithic reactor (400 cpsi) with the following inlet conditions: 5000 ppm CO, 2500 ppm O₂, N₂ balance, GHSV = 30000 1/h. Simulations using DETCHEM°geo [7].

**Fig. 2:** CH₄ oxidation light-off curves. Monolithic reactor (400 cpsi) with the following inlet conditions: 3000 ppm CH₄, 6000 ppm O₂, N₂ balance, GHSV = 30000 1/h. Simulations using DETCHEM°geo [7].

### Conclusions
- When the \( F_{\text{cat/geo}} \) value is derived from the characterization of the fresh catalyst, the model predicts ignition at much lower temperature than experimentally observed.
- The adjustment of \( F_{\text{cat/geo}} \) is not sufficient to well reproduce the light-off curve in the whole range of temperatures.
- When the kinetic dynamics is not well reproduced, modiﬁcations of the reaction pathways and kinetic parameters are needed.

### Outlook
- Improvement of the high temperature area may be sensibly reached via implementation of transient plug-ins available in DETCHEM package.
- Assess other microkinetic mechanisms to verify the impact of alternative reaction pathways and DFT-based kinetic parameters.
- Operando studies within CRC-1441 project are going to provide models to forecast the structural changes of the catalyst, enabling a fair description of the particles through values of \( F_{\text{cat/geo}} \) linked with the dynamic structure.

### References and Acknowledgements

**References**

**Acknowledgements**
The work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – CRC 1441 – Project-ID 426888090.

We thank Joachim Ceschelovsky and Marta Cazusa for sharing the experimental light-off data within CRC 1441.